

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
15 November 2001 (15.11.2001)

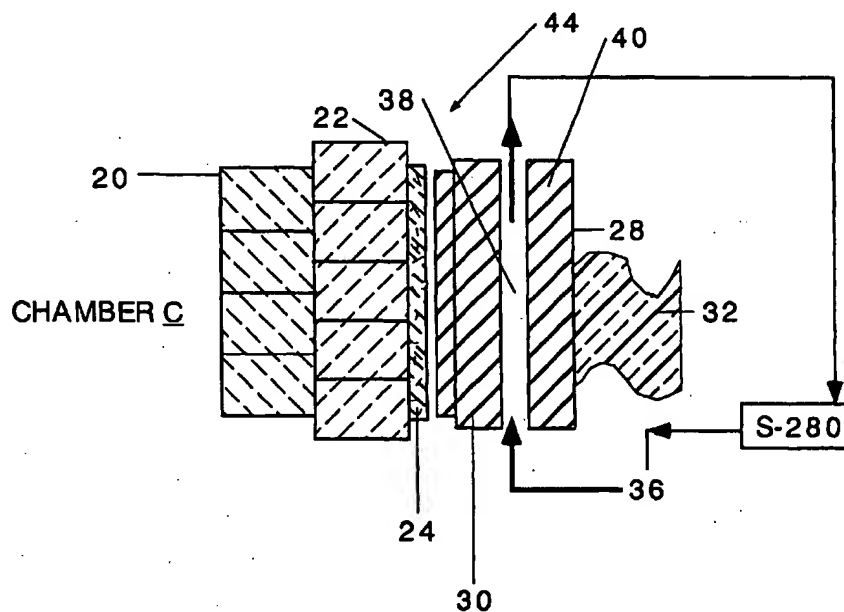
PCT

(10) International Publication Number  
**WO 01/86220 A2**

- (51) International Patent Classification<sup>7</sup>: **F27D** (74) Agent: **MILLER, William, B.**; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).
- (21) International Application Number: PCT/US01/14595
- (22) International Filing Date: 4 May 2001 (04.05.2001) (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 09/565,826 5 May 2000 (05.05.2000) US (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **THE DOW CHEMICAL COMPANY** [US/US]; 2030 Dow Center, Midland, MI 48674 (US).
- (72) Inventor; and  
(75) Inventor/Applicant (*for US only*): **JEWELL, Dennis, W.** [US/US]; 209 Coleman Drive, Angleton, TX 77515 (US).
- Published:  
— *without international search report and to be republished upon receipt of that report*

[Continued on next page]

(54) Title: REFRACTORY PRESSURE VESSEL



(57) Abstract: A reactor for gasifying carbonaceous materials including an interior lining of one or more refractory materials, a pressure vessel enclosing the refractory lining, preferably a corrosion resistant cladding lining the pressure vessel and one or more channels for circulating a heat transfer fluid substantially jacketing the pressure vessel to control pressure vessel wall temperature and preferably also lining temperature during down time.

WO 01/86220 A2



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## REFRACTORY PRESSURE VESSEL

The invention relates to a refractory vessel for gasifying carbonaceous materials, and  
5 more particularly to a vessel wall construction and temperature control system.

Related inventions include a prior patent application for a Method and Apparatus for  
the Production of One or More Useful Products from Lesser Value Halogenated Materials,  
PCT international application PCT/US/98/26298, published 1 July 1999, international  
publication number WO 99/32937. The PCT application discloses processes and apparatus  
10 for converting a feed that is substantially comprised of halogenated materials, especially by-  
product and waste chlorinated hydrocarbons as they are produced from a variety of chemical  
manufacturing processes, to one or more "higher value products" via a partial oxidation  
reforming step in a gasification reactor.

Gasification is in this regard a well-known technology for consuming by-product and  
15 waste carbonaceous materials and producing useful, more valuable products therefrom.  
The related application of the preceding paragraph provides a new approach to the treatment  
of a particular class of carbonaceous materials and wastes now predominantly processed in  
liquid thermal oxidation facilities – namely, halogenated materials and especially by-product  
and waste chlorinated hydrocarbons. The refractory pressure vessel of the present invention  
20 is considered to be especially useful in this particular context, but finds utility also in the  
gasification of other carbonaceous materials.

Gasification offers several potential advantages to liquid thermal oxidation,  
including lower economic costs, reduced emissions and capture of maximal chemical values  
of the feed stream constituents. In relation to the particular context of processing  
25 halogenated carbonaceous materials, gasification is also more flexible than other competing  
halogenated material waste treatment technologies (that is, other than liquid thermal  
oxidation), in that gasification is suited to working with a significantly broader range of  
acceptable feedstock compositions.

An illustrative embodiment of a gasification process, in particular for halogenated  
30 materials, is reviewed below in conjunction with an illustrated block flow diagram of Figure  
1. Within a gasification process, gasification typically occurs at partial oxidation conditions,  
that is, at oxygen to fuel ratios that are substoichiometric, with an excess of hydrogen.  
Reaction temperatures are typically greater than 1200°C and more typically greater than

1400°C, and reaction pressures are typically around 5 bars, gauge (barg). At these conditions the halide content of halogenated organic material should be converted to its gas phase hydrogen halide form.

Halogen halides, as a rule, are very corrosive in both the gas phase as well as the condensed aqueous phase. The dry gas phase corrosion rate of most materials of construction in contact with hydrogen halides increases exponentially with temperature. Aqueous hydrogen halide corrosion rates for materials also increase with temperature, but are exacerbated by the presence of oxygen or oxidizing metal salt species. The aggressive nature of the hydrogen halides, thus, as an example, emphasizes the need for specific attention in the design of safe and reliable pressure vessels for gasification reactor service.

In the field of the gasification of hydrocarbonaceous as opposed to halogenated feeds, two principal refractory vessel designs have been used. A "hot wall" design, illustrated in Figure 3, employs one or more layers of refractory, for example, hot face 20, insulating refractory 22, ceramic fiber paper 24, and optionally castable or plastic refractory 26, which collectively simply limit heat transfer from a reactor chamber C to an outside vessel wall 28, which might be a carbon steel shell, teflon lined or lined with Hastelloy Alloy B-2(ID), and ultimately limit heat loss to the atmosphere A. This design provides no positive means of controlling vessel wall temperatures themselves. The result is that vessel wall temperature can vary widely with operating conditions, refractory integrity and ambient conditions. One aspect of the present invention is to improve upon such design, finding the design particularly not optimal for use in gasifying halogenated organic materials, primarily because it lacks positive wall temperature control and the degree of influence over hydrogen halides-related corrosion of the vessel wall afforded by such control.

A second design used in refractory wall construction for the gasification of hydrocarbonaceous materials, the interior "membrane wall" design, is illustrated in Figure 4. The interior "membrane wall" design again employs one or more layers of a refractory 20, 22, 24 and optionally 26 within a so-called membrane 34 located within the pressure vessel 28. This membrane is constructed of any number of conduits or passages 38 (usually tubes) for circulating a fluid heat control substance 36. The conduits together make up an interior "membrane" barrier. The membrane and refractory materials are all contained within the pressure vessel (typically leaving a small space between the membrane and vessel wall). The membrane may be made of any of various materials of construction. A heat transfer

fluid flows through the membrane conduits to absorb heat from the reactor chamber C, thereby limiting vessel wall temperatures. Internal membrane systems, which do provide a measure of control over vessel wall temperatures, have other disadvantages which include high costs of construction and maintenance in the harsh environment. The interior  
5 membrane design can be further complicated if a "gas-tight" design is desired, to minimize process gas migration to the pressure vessel wall. One aspect of the instant invention is to improve upon this interior membrane design for purposes of a reactor for the gasification of carbonaceous materials, in particular of halogenated materials whereby one or more hydrogen halides result. The interior membrane design is unsuitably complex and  
10 expensive, both in construction and in maintenance, the latter aspect being particularly critical for service in a harsh hydrogen halide gasification environment.

Jacketing techniques are known. Such are described, for instance, in R.E. Markovitz, "*Picking the Best Vessel Jacket*", Chem. Engr. pp 156-162, Nov. 15, 1971; R.E. Markovitz, *Chapter: Heat Transfer: Jacketed Vessels in Heat Transfer Design Methods*, ed.  
15 J.J. McKetta, Marcel Dekker, 1991; W.R. Penney, Section 3.14 (3.14.1, .2 and .3) in: *Hemisphere Handbook of Heat Exchanger Design*, G.F. Hewitt, ed. 1981; I.H. Lehrer, "*Jacket-Side Nusselt Number*", IEC Proc. Des. Dev., 9 No. 4, pp 553-558, 1970; J.A. Kaferle, Jr. "*Calculating Pressures for Dimple Jackets*", Chem. Engr., pp 86, November 24, 1975. However, conventional applications for jacketed reactors have been directed to  
20 controlling the heat transfer to or from a reactor itself, often a liquid phase reactor, in order to control the temperature of the reaction itself, or of the vessel contents. In contrast to the above, the instant inventive design teaches a jacketed reactor for use with the gasification of carbonaceous materials and in particular halogenated materials. The temperature-controlled jacketed gasification reactor of the instant invention is not structured or designed to control  
25 the bulk temperature of the contents of the reactor itself. Rather the function of the jacket design is to control and limit the temperature of the pressure vessel walls and cladding, if used, separately from and essentially independently of, and substantially below normal operational levels of the temperature in the reaction chamber and its contents, *per se*.

Thus, while current gasification practice typically uses either a "hot wall" concept  
30 with a suitable material or lining for expected corrosion conditions, or an interior "membrane wall" for managing heat loss through the refractory system to the pressure vessel wall, the present invention serves both of those functions while being unique in a

number of aspects. The new externally jacketed reactor is designed with heat transfer fluid circulation for wall temperature control, including cooling during operations and also preferably heating during down time. This wall temperature control system can limit the maximum or high wall temperature, thus limiting hot dry gas corrosion. Because high  
5 levels of hydrogen halide are contemplated in a process according to the above-referenced, related PCT application, and because gas phase corrosion rates of materials such as HCl rise exponentially with temperature, disciplined wall temperature control is very important.

High wall temperature can occur due to high ambient temperatures, high internal gasifier operating temperatures, or gas permeation or "by-passing" of the refractory such  
10 that gas contacts the vessel wall. These "hot-spots" are not uncommon in large, refractory lined vessels. For these reasons, simple hot wall designs, as discussed above, are believed inferior for long term gasifier service. Furthermore, wall temperature control can be extremely important during stand-by, start-up, heat-up, degradation, or shut-down run conditions for a gasifier, especially a gasifier for halogenated materials. The wall  
15 temperature control of the instant invention is also preferably designed to prevent cold or wet aqueous acid, in particular hydrogen halide, condensation. Aqueous acids or hydrogen halides are very corrosive. Preventing this condensation is critical for optimal corrosion control for most materials of construction. When using either prior art hot wall or internal membrane systems, these "cold" conditions could occur, due to cold ambient conditions,  
20 precipitation, or at local cold spots characterized by high heat loss (for example, at burners, pressure vessel heads). Disciplined wall temperature control, thus, is also extremely important to prevent wet aqueous hydrogen halide condensation and the corrosion associated therewith.

The new jacketed vessel construction of the instant invention can also eliminate  
25 problems with crevices and stress points inherent in membrane designs. The membrane design is typically fabricated from bent and welded tubes or channels. This bending, fabrication and welding process inevitably results in residual material stresses, and will also have some crevices. These higher stressed areas and crevices result in higher local corrosion rates in the membrane material. A refractory pressure vessel externally jacketed  
30 for temperature control provides a simpler, cheaper construction and maintenance program compared to that for an internal membrane design and promises greater reliability. An internal membrane wall requires that many panels or components be assembled inside of the

pressure vessel. To allow for future repairs, these pieces are typically fabricated small enough to pass through vessel manways. These pieces must be assembled inside the vessel. Interior membrane design, thus, is quite complex, requires appropriate strength to support the weight of all refractory and is further complicated in that it must allow for thermal growth differences between refractory, the membrane wall, and the pressure vessel shell. With the possibility for achieving a more uniform wall temperature by an exterior temperature-controlled jacketed vessel, thermal growth differences can be minimized.

Further, the number of pressure vessel penetrations is limited with an exterior temperature-controlled jacketed reactor design, as compared to the interior membrane wall design. The interior membrane wall requires numerous nozzles for coolant inlet and outlet. These vessel wall penetrations offer undesirable points of stress and crevice corrosion for the pressure vessel. In contrast, the smooth simple internal shapes possible with an exterior temperature-controlled jacketed pressure vessel may be clad, lined, or coated with a wide variety of materials, simply and economically.

Further again, since an exterior temperature-controlled jacket design system tends to provide a more uniform temperature (and thus better corrosion control) across exposed surfaces, the external temperature controlled jacketed reactor design can reduce the necessity for inert gas purges, as per those that would be necessary for the gas spaces or chamber behind an interior membrane wall design. These purges are undesirable gas diluents.

The invention comprises a reactor for gasifying carbonaceous materials, and in particular halogenated materials. The reactor includes an interior lining of one or more refractory materials defining a reactor chamber, a pressure vessel enclosing the refractory lining and reactor chamber and one or more channels defined about the pressure vessel and substantially surrounding or encompassing the enclosed reactor chamber, and through which a heat transfer fluid may be circulated. The one or more channels are connected to a heat transfer fluid circulation system. Thereby, pressure vessel and also preferably lining wall temperatures can be controlled. Operationally, when the reactor chamber temperature is high, the circulation system will be operated to cool the vessel wall, or maintain the vessel wall temperature below certain desirable limits. When the reactor is not running, the circulation system can be operated to heat the reactor chamber lining above a minimal

desired temperature. Preferably a corrosion resistant cladding lining the pressure vessel is included.

The invention includes methods for gasifying a carbonaceous feed including halogenated materials in a reactor which comprises a first pressure vessel lined with a refractory material, comprising the steps of feeding the carbonaceous feed and oxygen to the reactor under reducing conditions so as to produce products therefrom including a synthesis gas, and circulating a heat transfer fluid in contact with outside first pressure vessel wall portions such that the fluid maintains an exterior reactor wall temperature over at least the outside first pressure vessel wall portions which is below a target level, the target level being substantially below operational reactor temperatures and preferably being within a range of approximately 150°C to 250°C.

A better understanding of the present invention can be obtained when the following detailed description of the preferred embodiment is considered in conjunction with the following drawings, in which:

Figure 1 is a block flow diagram of a preferred embodiment of a gasification process, to which the instant invention applies.

Figure 2A details more specifically features of a gasifier found in Figure 1.

Figure 2B illustrates a heat transfer fluid control system useable with a gasifier of Figure 2.

Figure 3 illustrates a prior art hot wall concept for a reactor vessel.

Figure 4 illustrates a prior art concept of an internal membrane wall reactor vessel for a gasifier.

Figures 5A-5F illustrate an integrally jacketed vessel of the instant invention, illustrating a vessel within a vessel concept, with one or more channels being defined by various means including by dimpling or baffling.

Figures 6A-6D illustrate an external membrane wall or a panel embodiment of the instant invention, with channels defined by coil type structure.

Figure 7 illustrates jacket zone arrangements.



An embodiment of a preferred, illustrative gasification process for halogenated materials of a type more particularly described in our related PCT application ("Method and Apparatus for the Production of One or More Useful Products from Lesser Value

- 5 Halogenated Materials", PCT international application PCT/US/98/26298, published 1 July 1999, international publication number WO 99/32937) will be discussed briefly, offering a prime application for the instant invention. Such gasification process can be viewed as comprised of a number of major processing areas, as illustrated in the block flow diagram of Figure 1.

- 10                   1) Gasifier 200  
                  2) Quench 300  
                  3) Particulate Removal and Recovery 350  
                  4) Aqueous HCl Recovery and Clean-up 400, 450  
                  5) Syngas Finishing 700

- 15 For purposes of the following discussion the hydrogen halide produced will be assumed to be HCl.

The gasifier area 200 of a preferred embodiment, as more particularly illustrated in Figures 2A and 2B, consists of two reaction vessels, R-200 and R-210, and their ancillary equipment for the principal purpose of reforming the halogenated material, typically RCl's.

- 20 In this embodiment, the halogenated feed (stream 144) is atomized into a primary reactor R-200 with oxygen 291 and steam 298. In a harsh gasification environment, the RCl or the like components are partially oxidized and converted to carbon monoxide, hydrogen chloride, hydrogen and lesser amounts of water vapor and carbon dioxide, with trace amounts of other substances including soot (being essentially carbon). The products from
- 25 R-200 preferably flow into a secondary reactor R-210, where all reactions proceed to completion, thus yielding high efficiencies for all halogenated species and tending to minimize undesirable side products such as soot.

- Because of the corrosive nature of hydrogen halides, or HCl, both as a hot, dry gas and as a condensed liquid, the reactor vessel shells and connecting conduit are preferably
- 30 "jacketed", as discussed more fully below in accordance with the instant invention. The jacketing creates one or more channels connected to a closed heat transfer fluid system S-280, illustrated in part in Figure 2B.

To continue through the gasification system of the block flow diagram of Figure 1, hot gases from the reactor R-210 are preferably cooled in a quench area 300 by direct contact with a circulating aqueous stream. Reactor effluent or product gas and the aqueous stream can be intimately mixed in a quench vessel. The mixture can then flow to a vapor-liquid separator drum from which a quenched gas can pass overhead and a bottoms liquid can be cooled and recycled to the quench.

Particulates in the product gas from a reactor system, including for example soot, can be scrubbed from the gas stream in a scrubber in particle recovery stage 350. The gas from the scrubber is preferably then introduced to a hydrogen halide or HCl absorption column 400. Noncondensable components can pass through the absorber overheads and on to a syngas finishing area 700. HCl in the gas from the scrubber can be absorbed to provide an aqueous acid bottoms stream. This aqueous acid stream can be filtered and passed through an acid cleanup unit 450 to remove final traces of particulates and organics, yielding a product grade aqueous HCl product. The product can be sold as is, or further processed to yield anhydrous HCl as desired (the suitable steps and apparatus for doing so being taught in the prior application). A caustic scrubber and syngas flare system are included in a syngas finishing area 700.

Having reviewed an embodiment of a gasification process for halogenated materials, we return now to review gasifier 200 in more detail, as illustrated in Figure 2. Gasifier area 200, in the embodiment as discussed above, consists of two reaction vessels R-200 and R-210 and their ancillary equipment for the principal purpose of halogenated feed material reformation. For the purposes of this discussion the halogenated material will be assumed to comprise chlorinated organic materials (RCl's).

Primary gasifier R-200, in the preferred embodiment illustrated, functions as a down fired, jet stirred reactor, the principal purposes of which are to atomize the liquids fed to R-200, evaporate the liquids, and thoroughly mix the vaporized feed with oxygen, moderator, and hot reaction products. The gasifier preferably operates at approximately 1450°C and 5 bars gauge (75 psig). These harsh conditions tend to insure near complete conversion of all feed components in R-200.

In order to prevent unwanted corrosion of a gasifier shell in the above embodiment, from either hot, dry hydrogen halide corrosion or from the condensation of aqueous

hydrogen halide, the instant invention discloses providing a gasifier shell that is jacketed for pressure vessel wall temperature control.

A portion of this jacketing system providing heat transfer fluid circulation to a channel or channels defined by the jacket for wall temperature control is illustrated in Figure 2B. System S-280 includes a cooler E-280, surge drum D-280, and pumps P-280 for circulating a heat transfer fluid, preferably Dowtherm GRP or Syltherm 800, but possibly being other fluids including water. Hot, refractory-lined gas vessels and piping up to and including a quench inlet are preferably completely jacketed. During normal operations cooling by a heat transfer fluid from fluid control system S-280 removes heat transferred from the gasification process chamber through refractory linings to the vessel shell and piping, typically steel shells. A small heater E-281 is also preferably provided to heat a heat transfer fluid to operating conditions from a cold start as well as for maintaining lining temperature during down times.

The temperature of a vessel shell will preferably be controlled at approximately 200°C, or between approximately 250°C and 150°C. The theoretical dewpoint of the hydrogen-halide containing gas mixture is approximately 130° -150°C. The true dewpoint however can be altered by the presence of salts, metals, or other corrosion products. Thus, the wall temperature is preferably maintained at a safe margin above the theoretical dew point. At temperatures exceeding 200°C, the dry gaseous HCl corrosion rate increases exponentially with temperature. It is therefore undesirable to heat the vessel shell walls more than necessary to prevent aqueous condensation. In preferred embodiments for operating the system, the jacketing system will attempt to control wall temperatures at all times, even downtime, except as necessary to perform system maintenance. Such control, even during down time, prevents atmospheric moisture from condensing as a corrosive liquid due to residual HCl or like substances in the system.

As discussed above, due to a potential extreme corrosivity of a high temperature gas mixture, as well as process condensate, the temperature of the reactor walls preferably receives constant control. To achieve constant and disciplined control of reactor wall temperatures under the extreme temperatures of a gasification reactor, the present invention discloses a refractory lined pressure vessel, preferably with careful selection of materials of construction to insure a reliably long life for the gasifier.

As discussed above, prior art "hot wall" concepts, illustrated in Figure 3, are not optimal and are possibly inadequate by themselves for controlling pressure vessel wall conditions for the gasification of carbonaceous materials, especially halogenated materials. Using the prior art hot wall concept, the wall temperature cannot be preferably maintained with sufficient discipline, including both above dewpoint and below desired maximum dry temperatures, at all times and across the range of ambient conditions necessary. For instance, gas by-passing behind refractory 20, 22, 24 and optionally 26 or a local refractory failure could overheat wall 28 resulting in excessive corrosion rates. Further, wall conditions during start-up, shutdown, idle periods and normal operation at cold ambient conditions cannot be controlled. Permitting such conditions and risks is not particularly desirable for a vessel operating at approximately 5 barg and especially if containing hot HCl-bearing syngas.

As discussed above, the prior art interior membrane design, illustrated in Figure 4, provides better wall temperature control than the "hot wall" concept of Figure 3, but is still not ideal. The membrane 34 presents significant complexity and challenges for the design and fabrication of the numerous panels and sections required to cover an entire vessel wall 28 area. The membrane 34 also poses substantial maintenance problems, requiring vessel entry, refractory removal, and possibly membrane panel removal for repair. Since the membrane must be of high alloy, this installation may be more expensive than the jacketed vessel design of the instant invention. The vessel 28 will require lining or cladding 30, or a complex chamber pad system with inert gas installed. This pad, typically  $N_2$ , is an undesired gas diluent. In some designs of the instant invention, such cladding may be foregone.

The jacketed shell of the instant invention, including an exterior channel or channels as illustrated in Figures 5-11, combined with a heat transfer fluid control system, as illustrated in Figure 2B, is a preferred design for gasifier vessels, in particular for halogenated material gasifier vessels. Such design provides a preferred level of wall temperature control, reliability and cost effectiveness. With the instant design a vessel wall temperature can also be maintained above dewpoint for essentially all operating modes. Even for gas bypassing, or for local refractory 20 and 22 failure, a jacketed heat transfer design provides an efficient, practical and disciplined cooling capability to limit wall temperatures.

Design alternatives for the jacketing as illustrated in Figures 5-11 include internal jacketing, external membrane wall or panels, welded "half-pipe," dimple jacketing, coil jacketing of the vessel, and external panels. Jacketing can be accomplished through a number of techniques. A temperature control jacket could be a "vessel in a vessel" design, illustrated in Figure 5 as well as Figure 2A. A heat transfer fluid 36 could be circulated through a channel or channels 38 defined by such jacket 40, which channel 38 might comprise simply a space created between two vessel walls. In such a space, as illustrated in Figure 5B, the heat temperature control fluid could preferably be introduced with tangentially oriented nozzles to impart a swirling flow pattern throughout the jacket. A plain jacket offers the simplest construction and thus potentially a lower initial cost. The plain jacket may be more suitable for condensing, heating media than for use with sensible fluids. One reason is that the relatively large passage results in low fluid velocities and correspondingly low heat transfer coefficients, which are basically determined by natural convection. The plain jacket amounts to a double wall on the reactor vessel. In particular, if sensible liquid heating or cooling is employed in a plain jacket design, the use of agitating nozzles are recommended, as illustrated in Figure 5B. Agitating nozzles 50 may be used to direct inlet fluid 36 more or less tangentially into a jacket 40, increasing the effective velocity and turbulence level. Then used with condensing media, impingement protection is highly recommended. Alternatives include the use of larger or multiple inlet nozzles.

Preferably a "jacket in jacket" design is used with internal baffling, illustrated in Figures 5C and 5D. This consists of a "vessel in a vessel" where the heat transfer fluid is circulated through chambers defined by two pressure vessel walls, interior pressure vessel wall 28 and jacket pressure vessel wall 40 and baffles 52. The fluid is circulated by a circulation control system to carefully control the velocity and heat transfer coefficient of the heat transfer fluid in order to maintain vessel walls and cladding within certain temperature ranges, substantially independently of the temperature within the reactor. Preferred conduit designs could balance between heat transfer coefficients and pressure drop considerations. Preferred baffles could be wound in a spiral or helix pattern around the reactor shell 28, for one preferred embodiment.

In general, a spiral plate baffle consists of a spiral strip welded edgewise to the pressure vessel shell. This forms a baffle which causes the jacket fluid to flow around the vessel in relatively small passages. There will inherently be some clearance between the

edge of the baffle and the inside of the jacket, through which some fraction of the circulating fluid can bypass. Otherwise, the jacket can be treated much like a coil.

A dimpled jacket, Figure 5E and 5F offers a variation on the baffled jacket design. As illustrated in the Figures 5E and 5F, an outer shell 40 is fitted with regular indentations 54 of the shell material. These dimples 54 are applied in regular pattern and are intended to induce turbulence. Dimples 52 are welded to vessel wall 28.

Another jacketing technique could use a membrane wall, a "half-pipe" jacket, or a plate coil approach, illustrated in Figures 6A-6D. For the half pipe design, Figures 6B and 6C, numerous half-pipe conduits 56 could be welded to a vessel shell 28 making parallel passages 38 for heat transfer fluid 36 flow. Outlets 58 and inlets 58 would be provided to circulate heat transfer fluid 36. Heat control coils 260, Figure 6A, such as used in an interior membrane system, might also be employed as an external jacket 40. Typically a half pipe jacket consists of a pipe split in half longitudinally and then welded to the shell. This design favors the situation where high jacket pressures are required, but it is an expensive method because it requires two long welds along each edge of the cut pipe. Heat transfer is well defined, since the geometry is known and no bypassing is possible. The half pipe jacket is better suited for sensible liquids such as water or other similar heat transfer fluids.

A plate coil of the weld-on variety as illustrated in Figure 6D is also possible, with embossing to create fairly well-defined flow channels. A clamp on plate coil might be used as well, being attached by clamping rather than by spot welding to the vessel.

As illustrated in Figure 7, jackets may be divided into several sections, each having a separate inlet and outlet. These zones can be used to advantage in critical applications to improve temperature uniformity in the vessel to remove condensate more rapidly from all the areas of the jacket when a condensing medium is used, to decrease the temperature change in a sensible medium, to control weld temperature in any vapor spaced area and to keep the jacket pressure drop within allowable values.

In accordance with the instant inventive design, cladding the pressure vessel wall may be desirable. Non-metal claddings for the gasifier vessel are not a preferred design, as they may be insufficiently "tough" to provide long service life. Refractory thermal movement and local hotspots due to refractory failure or gas bypassing may breach the

integrity of presently known non-metal linings. Therefore, a high alloy corrosion resistant metal cladding 30 will preferably be used in current preferred embodiments.

In operation, as discussed above, inside vessel wall portions are preferably maintained at or slightly above 200°C to remain above the gas dewpoint. Bulk HCl gas dewpoint is estimated in the 130 - 150°C range, but local dewpoint elevation due to metal corrosion products dictates the higher operating temperature. Such considerations suggest a preferred use of a high temperature, synthetic heat transfer fluid, such as a Dowtherm A, in circulation path 38. High temperature stability of the fluid is important to minimize the effects of local hotspots on long term fluid stability and temperature control. Fluid properties and shell failure scenarios should dictate operating pressures of the jacket system.

Care should be exercised in the inclusion and design of nozzles and appurtenances on the gasifier pressure vessel. Shell penetrations should be minimized, and the necessary penetrations carefully jacketed and designed for temperature control.

The instant jacketed reactor design as illustrated in Figures 5-11, employs one or more interior layers of refractory 20, 22, 24 and optimally 26 suitable for exposure to hot raw gas, possibly hydrogen halide-containing gas, see Figure 5A. The one or more layers of refractory will typically include a "hot-face" refractory layer 20 for chemical resistance and an insulating refractory layer 22 for heat transfer control. High alumina refractory brick (more than 99 percent) with an insulating firebrick refractory is one option. This refractory system would be installed directly in a pressure vessel 28. External insulation 32 may also be included. Any number of corrosion resistant materials could surround the refractory layer to serve as cladding, if desired, and protect the pressure vessel wall against corrosive media. For instance, the vessel shell could be lined with plastic materials, ceramic, glass, or other coatings. Most preferably, however, the vessel wall would be clad with a metal in the form of a corrosion resistant alloy 30. The alloy provides the best combination of corrosion resistance and mechanical toughness. Other known lining alternatives could be subject to damage and gas permeation due to thermal movement of the refractory, or differential expansion between the lining and the steel shell. Hastelloy Alloy B3 and Hastelloy Alloy C-276 are two good cladding alternatives for the lining. Each provides good resistance to dry hydrogen halide corrosion and good corrosion resistance to aqueous hydrogen halide solutions. Hastelloy Alloy C-276 offers less resistance to pure aqueous hydrogen halide solutions but higher resistance to solutions with minor contaminants such as metal salts,

dissolved oxygen or similar. Use of a corrosion resistant alloy layer also allows the use of low alloy steel for the actual pressure vessel shell 28 construction.

Corrosion resistance and vessel integrity is further achieved in the instant invention by separately and independently (within limits, given the reactor temperature) controlling the temperature of the pressure vessel walls 28 and lining through the channel or channels 38 provided by an external jacketing system 40. By such means the pressure vessel wall and lining can be maintained above the condensation point of the vessel contents, plus a nominal margin of safety of typically 50°C. Securing such wall temperature control has the additional advantage that a cladding material can then be selected for maximum dry gas phase corrosion resistance.

In the instant invention, as discussed above, vessel well temperature control is accomplished by "jacketing" the vessel with one or more conduits 38 and circulating through these a temperature control medium 36. The conduit or conduits should be connected to a fluid circulation control system, as illustrated Figure 2B.

Preferred embodiments of the present invention could employ one or two phase heat transfer. A two-phase system requires a more sophisticated design and complex piping, but provides a very high heat transfer coefficient. A preferred design, as illustrated in Figures 2A and 2B, uses a simple single-phase heat transfer fluid. The heat transfer fluid can be water or any number of commercially available fluids such as Dowtherm® products or Therminol® products or similar. Important parameters to consider in fluid selection concern the physical properties and behavior of the fluid and their interaction with the design of the jacket. These properties include operating temperature, maximum temperature, minimum operating temperature, viscosity, density, vapor pressure, surface tension, thermal conductivity, fouling characteristics, and degradation products. Many of the factors to consider in selecting a heat transfer fluid are discussed in "Sizing Up Heat Transfer Fluids & Heaters", by G. E. Guffey II, Chemical Engineering, October 1997.

One preferred embodiment for a heat transfer fluid circulation system S-280 of the instant invention consists of a surge drum or tank D-280 for holding fluid inventory, a pump P-280 suitable for pressuring the fluid through the network and jacket(s), and heat exchanger H-280 for (1) rejecting heat to the atmosphere or another media during normal operating conditions and for (2) heating the heat transfer fluid to bring the system to operating conditions prior to introduction of halogenated organic materials. The system S-



280 can be furnished complete with appropriate instrumentation (not shown) to control the jacketed reactor surface temperature at the desired temperature given the status of the gasification reactor process in general.

The following example is provided for appreciation of the instant inventive design.

5 Example 1

The following feed streams were fed to a gasifier through an appropriate mixing nozzle:

	Chlorinated Organic Material:	9037 kg/hr
	Oxygen (99.5 percent v purity):	4419 kg/hr
10	Recycle vapor or moderator:	4540 kg/hr
	[58.8 wt percent water vapor, 41.2 wt percent hydrogen chloride]	

The resulting gasification reactions resulted in a synthesis gas stream rich in hydrogen chloride and chamber conditions of approximately 1450°C and 5 barg. In the present example, the reactor was lined with a 6" (15.24 cm) thick layer of hot-face high alumina refractory brick backed by 9" (22.86 cm) of insulating firebrick. This refractory installation limited heat loss to the vessel wall. The pressure vessel was a low-alloy steel clad with 3 mm thick Hastelloy C-276. The vessel included an integral jacket that covered essentially all vessel surface area. The jacket included internal baffling to direct fluid flow and control velocity and heat transfer coefficients. Typical limits were a minimum of 1 m/sec to minimize fouling and maintain an acceptable heat transfer coefficient. A maximum velocity of approximately 4 m/sec limited pressure drop to within acceptable bounds. The heat transfer fluid inventory was stored in a low-pressure tank. This tank may be padded with an inert gas to control pressure and exclude oxygen from the system. A typical flow of approximately 1200 gpm was pumped by a centrifugal pump through the jacket system. Fluid return from the jacket passed through a water-cooled heat exchanger for rejecting heat from the system. The heat exchanger exit was controlled at 200°C, which was approximately 50°C above the pure hypothetical condensation point of the vessel contents; 50°C was considered a safe margin to avoid the effects of contaminants that elevated the condensation temperature. The surface temperature was thus controlled near its target of 200°C.

The foregoing disclosure and description of the invention are illustrative and explanatory thereof, and various changes in the size, shape, and materials, as well as in the

details of the illustrated system may be made without departing from the spirit of the invention. The invention is claimed using terminology that depends upon a historic presumption that recitation of a single element covers one or more such elements, and recitation of two elements covers two or more of the specified element.

5

## WHAT IS CLAIMED IS:

1. A reactor for gasifying materials, the reactor comprising:  
an interior lining of one or more refractory materials;  
a first pressure vessel enclosing the refractory lining; and  
5 one or more channels for circulating a heat transfer fluid, the one or more channels substantially jacketing at least a portion of the exterior of the first pressure vessel and being connected to a heat transfer fluid circulation system structured to remove heat to limit vessel wall temperatures substantially below reactor temperatures.
- 10 2. The reactor of claim 1 wherein the one or more channels jacket substantially the entire refractory-lined volume of the first pressure vessel.
3. The apparatus of claim 2 wherein the circulation system is structured to add heat.
- 15 4. The apparatus of claim 3 wherein the circulation system and one or more channels are structured in combination with the reactor to control pressure vessel wall temperature during reactor operation to below a target operating maximum and to raise lining temperature during reactor shutdown to above a target minimum.
- 20 5. The apparatus of claim 1 that includes a corrosion resistant cladding lining the pressure vessel.
6. The apparatus of claim 1 that includes insulation exterior to the one or more  
25 channels.
7. The apparatus of claim 1 wherein the one or more refractory materials include a hot face refractory material inside of an insulating refractory material.
- 30 8. The apparatus of claim 5 wherein the corrosion resistant cladding comprises corrosion resistant metal alloy.

9. The apparatus of claim 5 wherein the corrosion resistant cladding includes a non-metal lining.

10. The apparatus of claim 1 wherein the one or more channels are defined at least in part by a second pressure vessel surrounding a first pressure vessel.

11. The apparatus of claim 10 that includes baffles between the second pressure vessel and the first pressure vessel.

12. The apparatus of claim 2 wherein the one or more channels are defined at least in part by a second pressure vessel surrounding a first pressure vessel.

13. The apparatus of claim 12 that includes baffles between the second pressure vessel and the first pressure vessel.

14. The apparatus of claim 2 wherein the one or more channels jacketing the first pressure vessel are formed by coils forming a jacket that covers a substantial portion of the exterior surface of the first pressure vessel.

15. The apparatus of claim 1 wherein the reactor includes a feed nozzle adapted to input a liquid halogenated material into the reactor and a gas output adapted to discharge gas from the reactor.

16. The apparatus of claim 1 wherein the one or more refractory materials include a hot face material adapted to face reactor temperatures of at least 1550°C.

17. A method for gasifying a carbonaceous feed including halogenated materials in a reactor which comprises a first pressure vessel lined with a refractory material, comprising the steps of:  
feeding the carbonaceous feed and oxygen to the reactor under reducing conditions so as to produce products therefrom including a synthesis gas, and

circulating a heat transfer fluid in contact with outside first pressure vessel wall portions such that the fluid maintains exterior reactor wall temperatures over at least the outside first pressure vessel wall portions within a range of 150°C to 250°C.

5           18.     The method of claim 17 that includes maintaining operational temperatures inside the reactor vessel between approximately 1300°C and approximately 1500°C.

          19.     The method of claim 17 that includes maintaining operational pressure inside the reactor vessel at approximately 5 barg.

10

          20.     The method of claim 17 wherein circulating a heat transfer fluid includes circulating the fluid in one or more channels created between the first pressure vessel and an outer jacket structure.

15           21.     The method of claim 17 wherein circulating a heat transfer fluid includes circulating the fluid between the first pressure vessel and a second pressure vessel.

          22.     The method of claim 17 that includes lining the first pressure vessel with a cladding material.

20

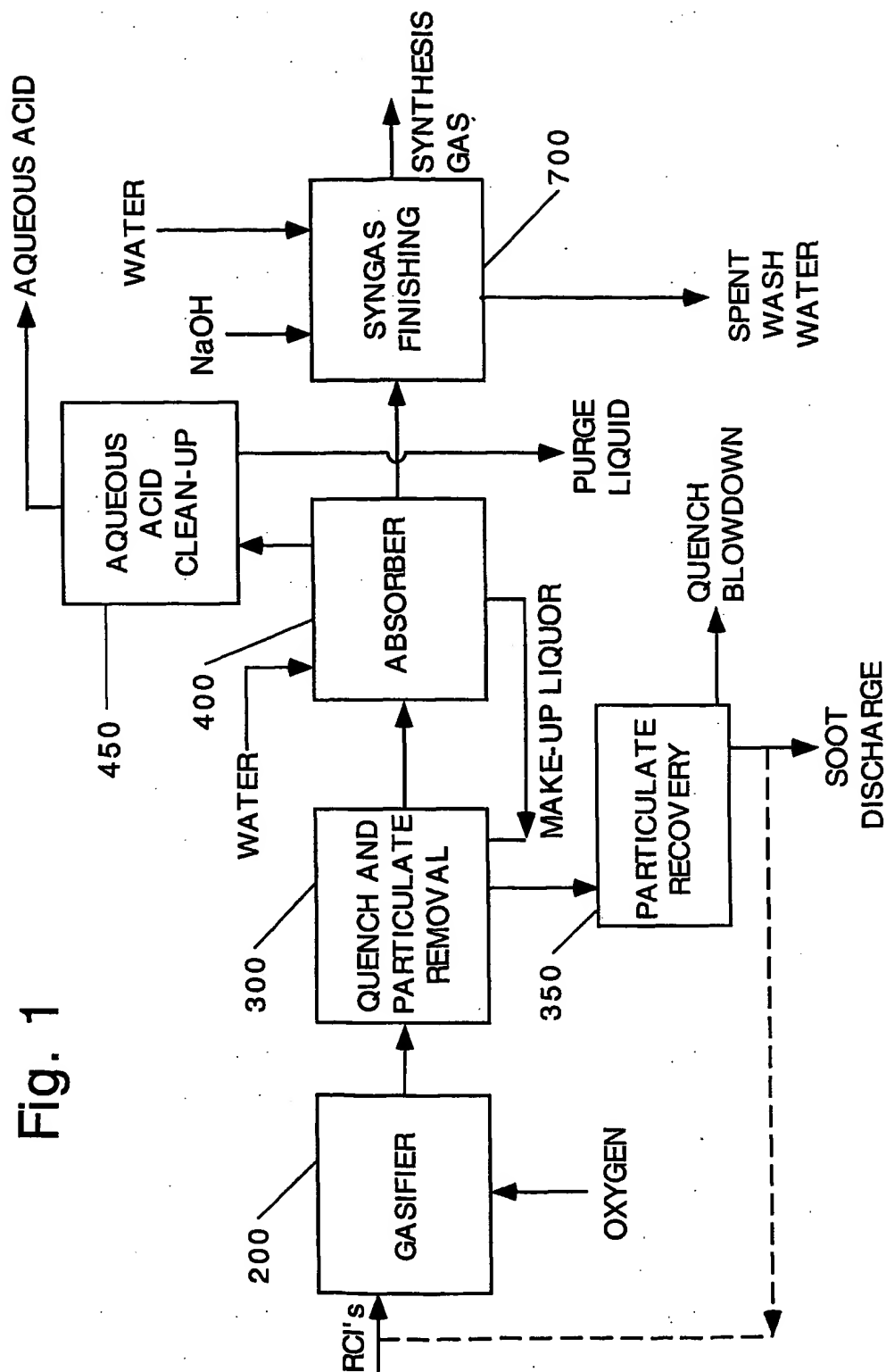
          23.     The method of claim 17 that includes maintaining lining temperatures above approximately 200°C when the reactor is not in operation.

          24.     The method of claim 17 that includes circulating a heat transfer fluid to cool  
25 first pressure vessel wall portions during reactor operation and to heat the reactor lining during reactor shutdown.

          25.     The method of claim 17 wherein the carbonaceous materials are halogenated materials.

30

1/9



2/9

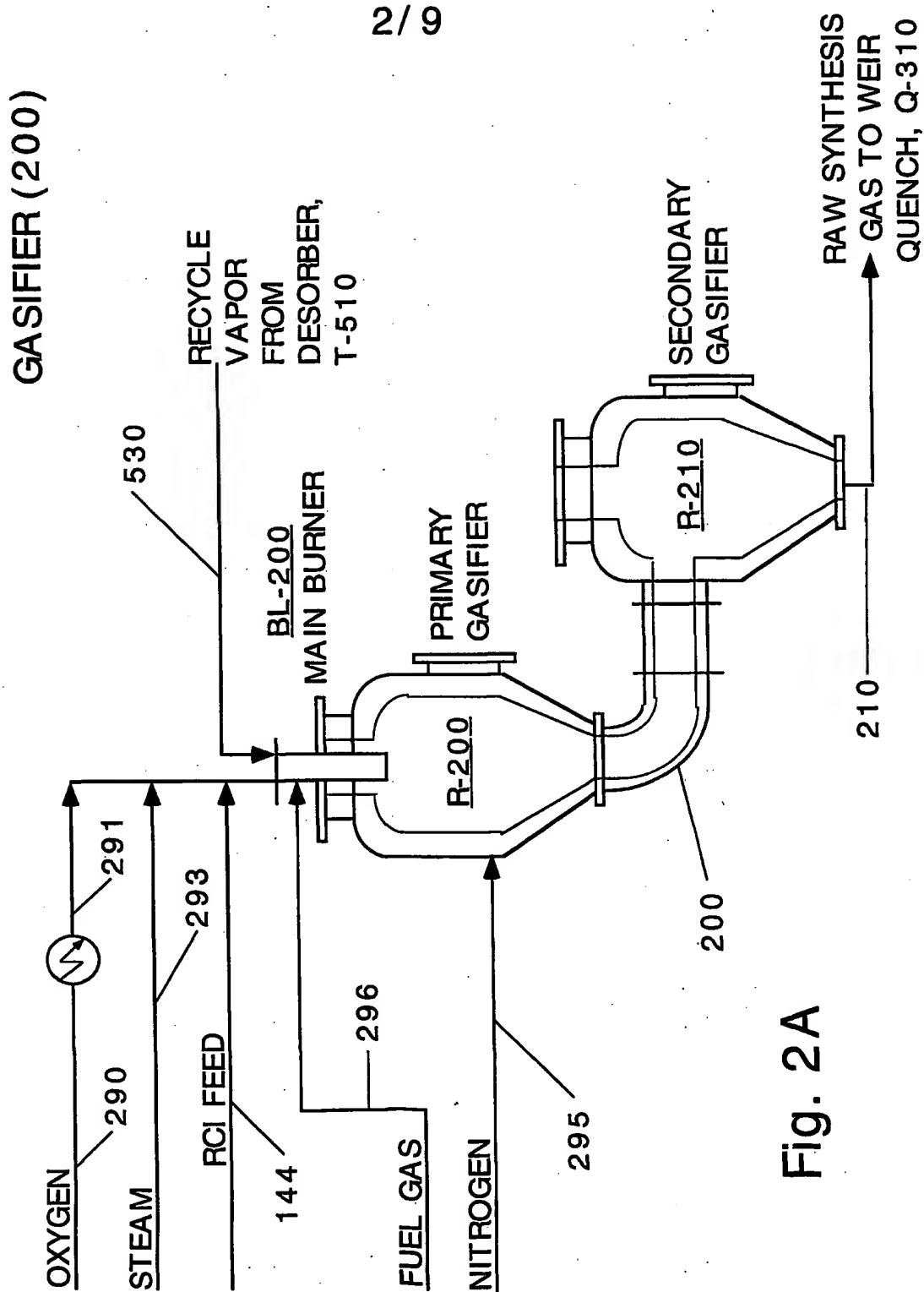


Fig. 2A

3/9

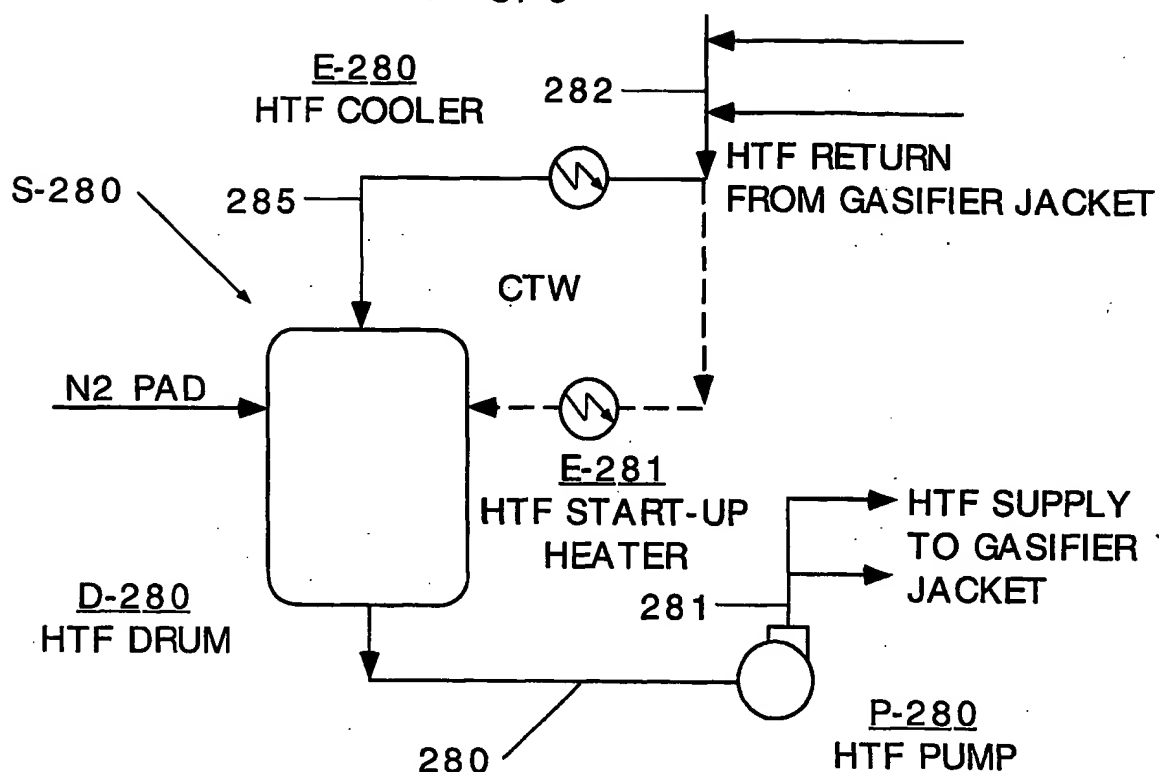


Fig. 2B

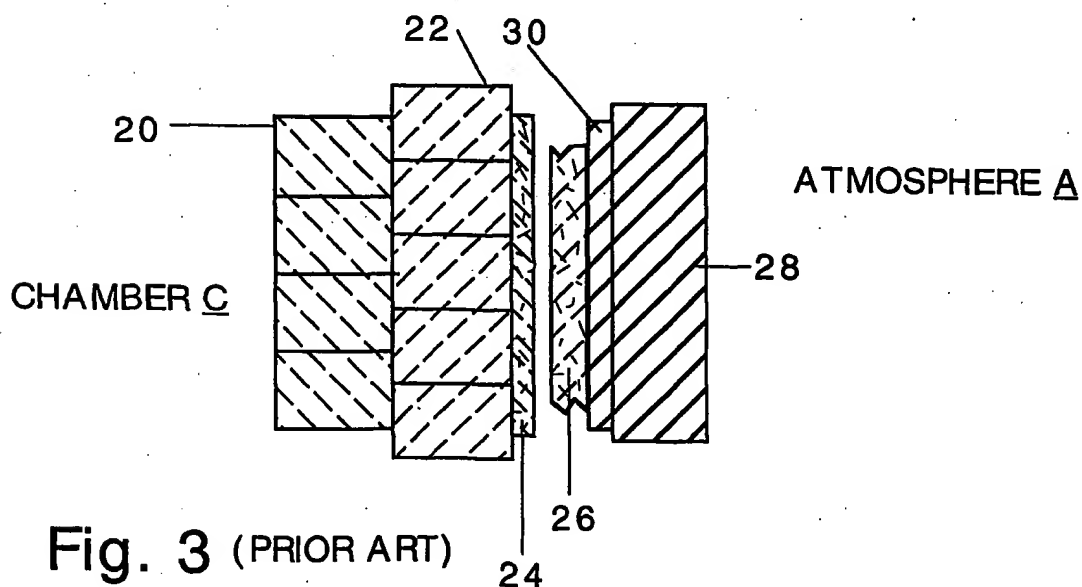


Fig. 3 (PRIOR ART)



4/9

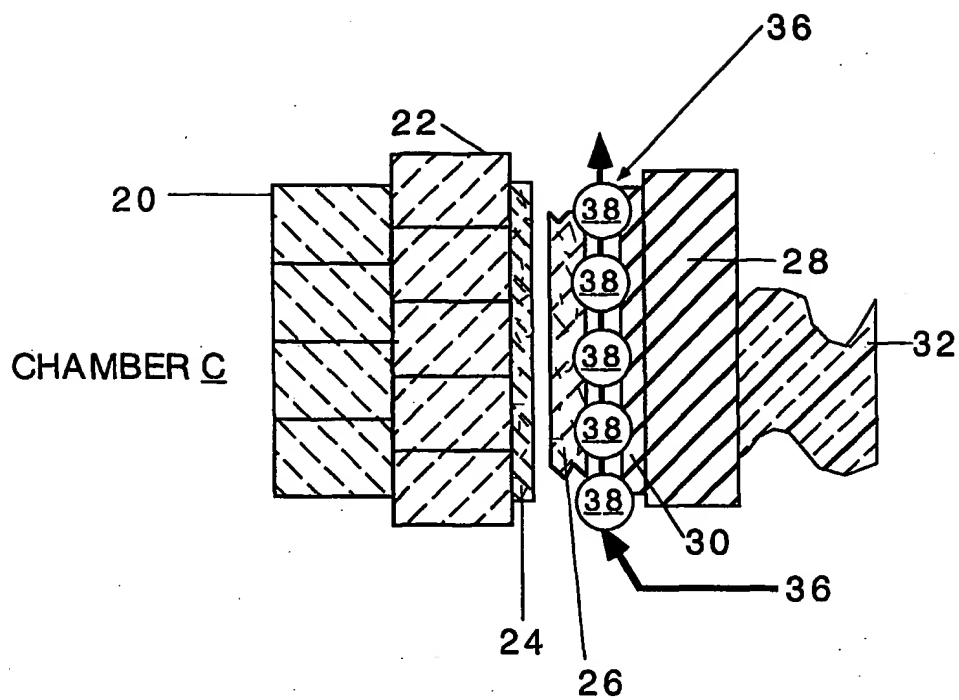


Fig. 4 (PRIOR ART)

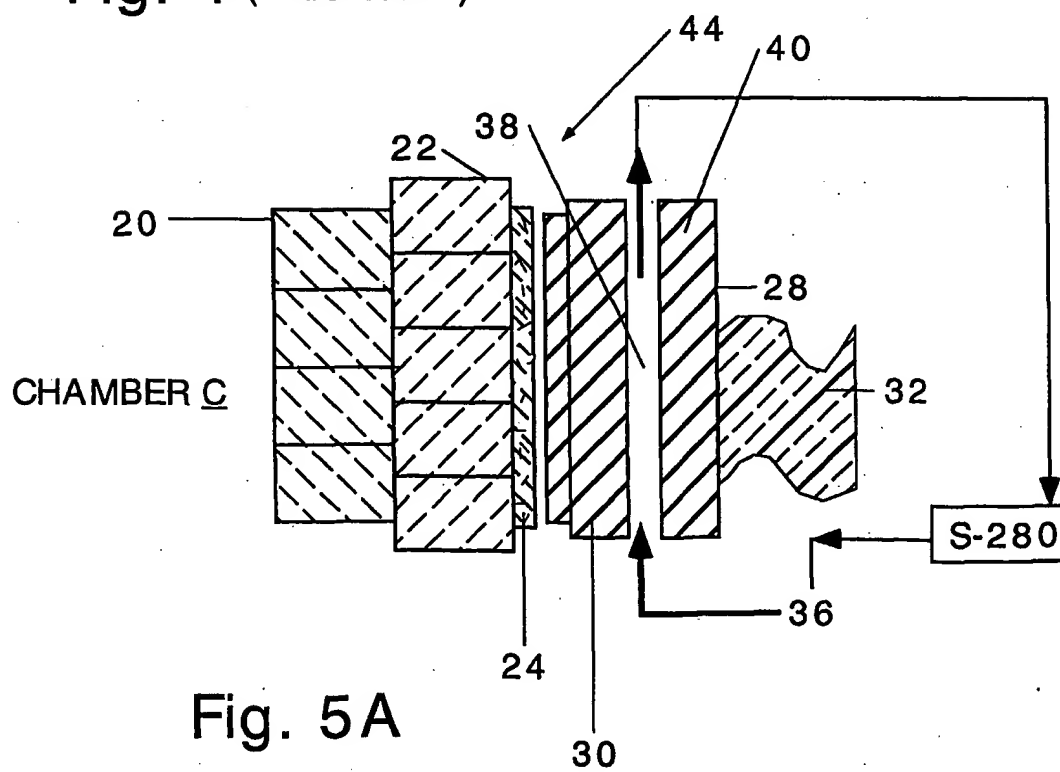
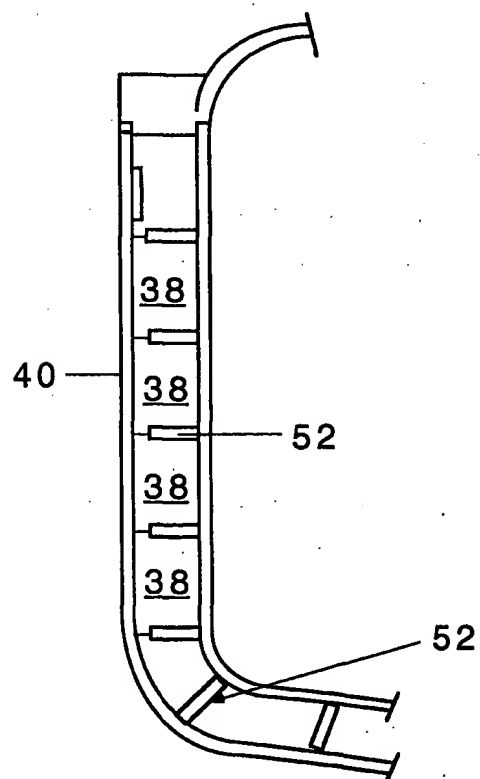
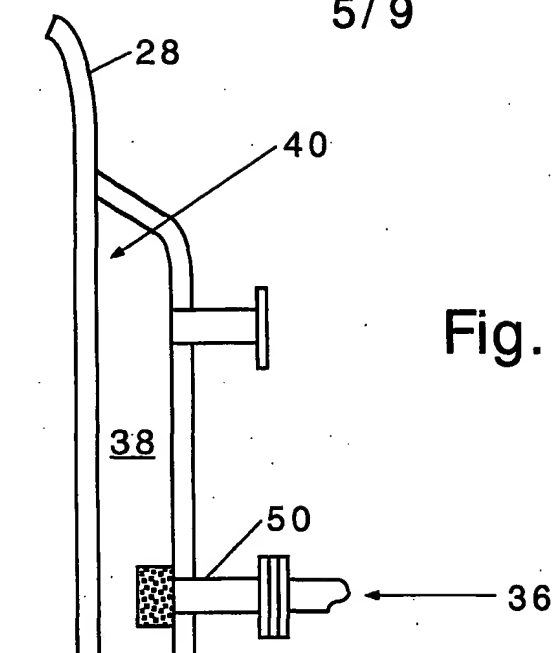


Fig. 5A

5/9



6/9

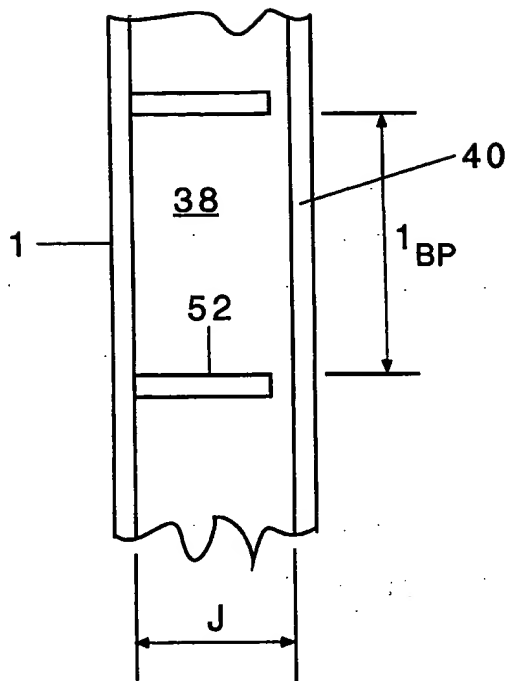


Fig. 5D

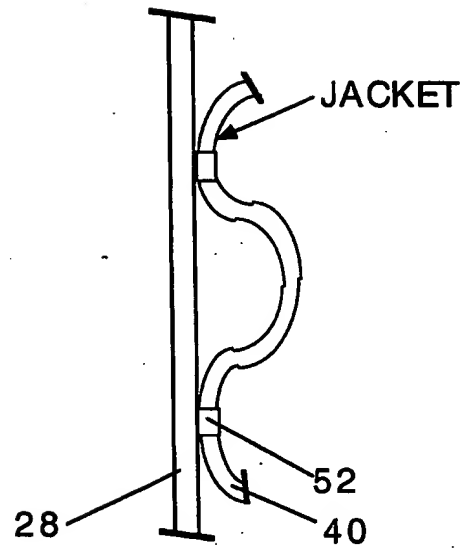


Fig. 5F

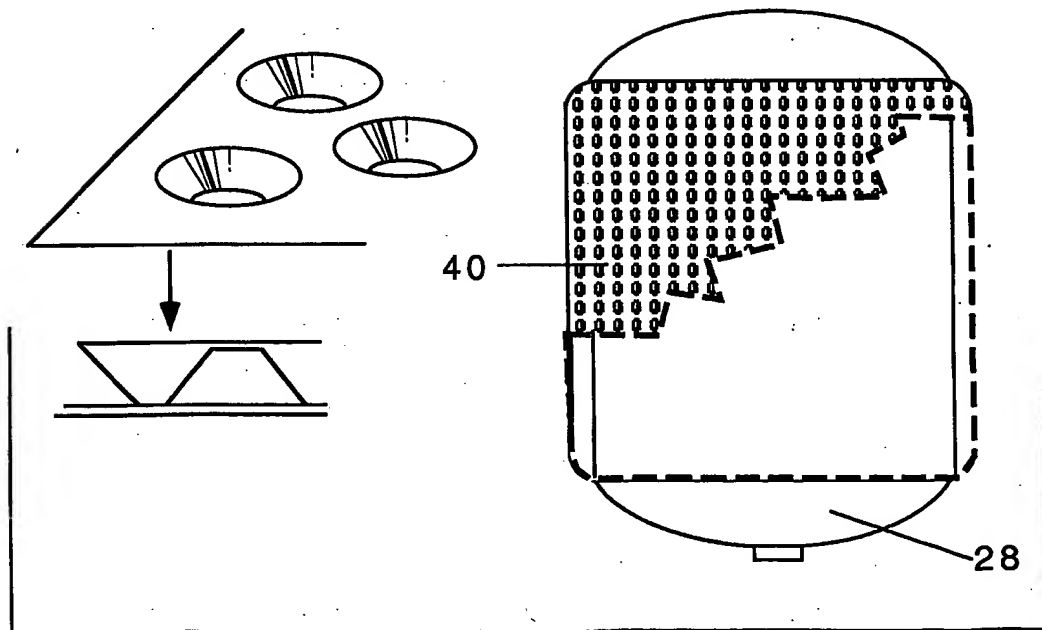


Fig. 5E

7/9

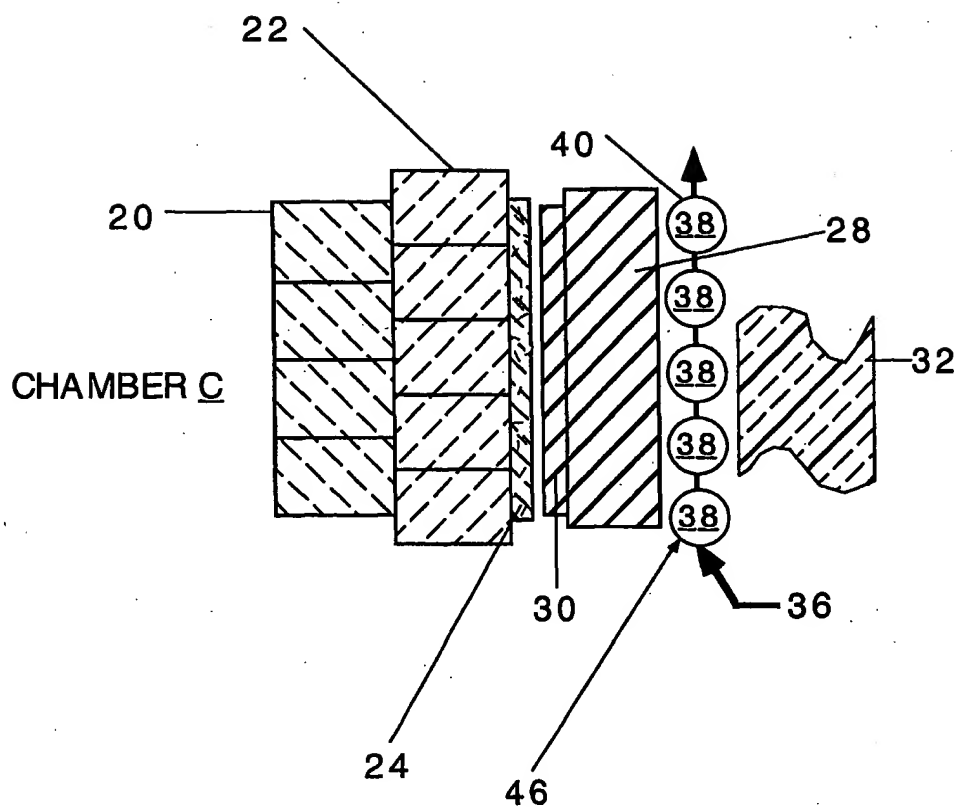


Fig. 6A

8/9

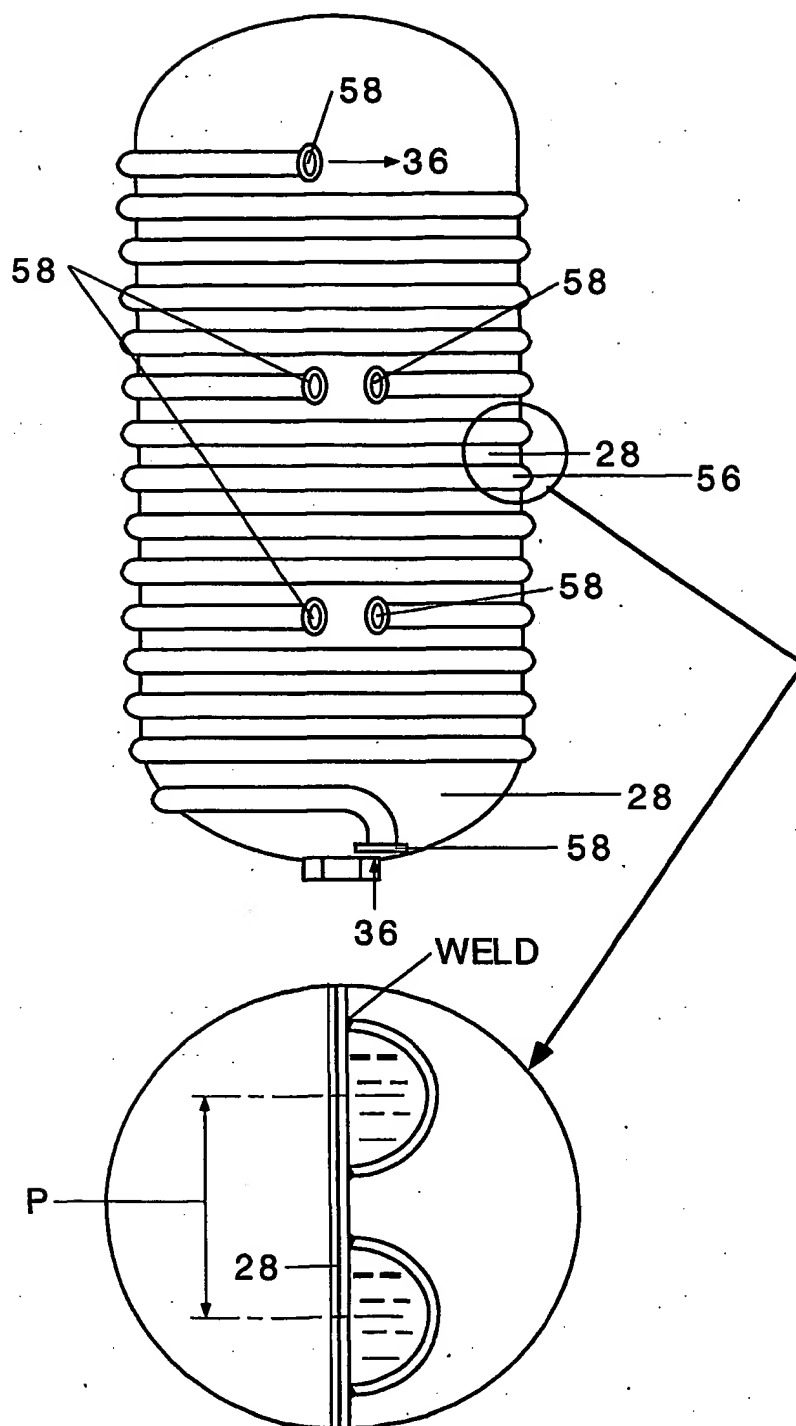


Fig. 6B

9/9

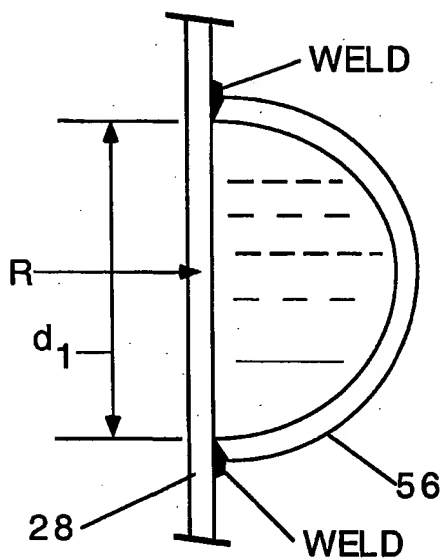


Fig. 6C

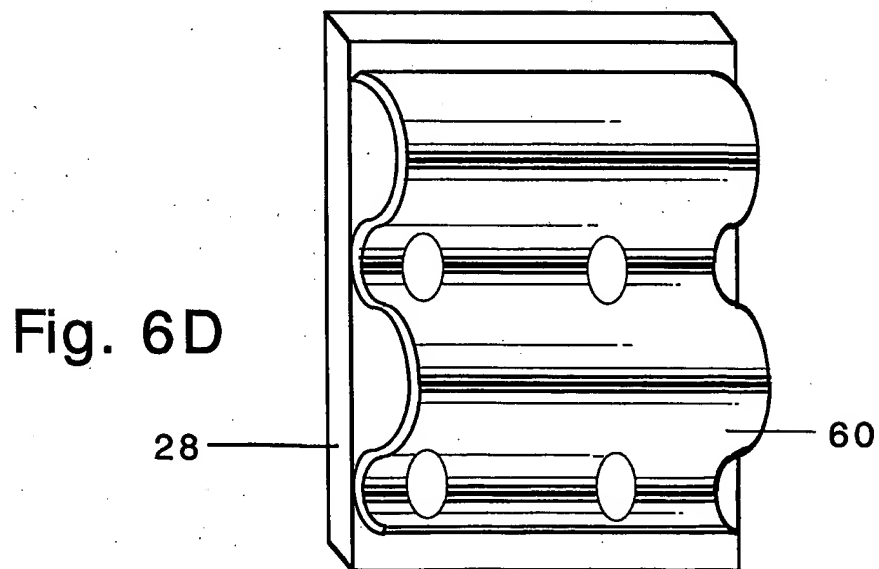


Fig. 6D